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# Calibration and use of the Chemcatcher<sup>®</sup> passive sampler for monitoring organotin compounds in water

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## ABSTRACT

An integrative passive sampler (Chemcatcher<sup>®</sup>) consisting of a 47 mm C<sub>18</sub> Empore<sup>™</sup> disk as the receiving phase overlaid with a thin cellulose acetate diffusion membrane was developed and calibrated for the measurement of time-weighted average water concentrations of organotin compounds [monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPhT)] in water. The effect of water temperature and turbulence on the uptake rate of these analytes was evaluated in the laboratory using a flow-through tank. Uptake was linear over a 14-day period being in the range: MBT (3–23 mL day<sup>-1</sup>), DBT (40–200 mL day<sup>-1</sup>), TBT (30–200 mL day<sup>-1</sup>) and TPhT (30–190 mL day<sup>-1</sup>) for all the different conditions tested. These sampling rates were high enough to permit the use of the Chemcatcher<sup>®</sup> to monitor levels of organotin compounds typically found in polluted aquatic environments. Using gas chromatography (GC) with either ICP-MS or flame photometric detection, limits of detection for the device (14-day deployment) for the different organotin compounds in water were in the range of 0.2–7.5 ng L<sup>-1</sup>, and once accumulated in the receiving phase the compounds were stable over prolonged periods. Due to anisotropic exchange kinetics, performance reference compounds could not be used with this passive sampling system to compensate for changes in sampling rate due to variations in water temperature, turbulence and biofouling of the surface of the diffusion membrane during field deployments. The performance of the Chemcatcher<sup>®</sup> was evaluated alongside spot water sampling in Alicante Harbour, Spain which is known to contain elevated levels of organotin compounds. The samplers provided time-weighted average concentrations of the bioavailable fractions of the tin compounds where environmental concentrations fluctuated markedly in time.

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## 1. Introduction

The organotin compounds, monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPhT) are considered among the most hazardous compounds of anthropogenic

origin that have been introduced into the aquatic environment. These compounds exhibit toxicity towards a variety of waterborne organisms at the ng L<sup>-1</sup> level [1]. Anti-fouling paints are one of the most important sources of TBT in the aquatic environment, with other inputs being derived from

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the use of certain bactericides and pesticides that contain this compound. MBT and DBT can be formed as environmental degradation products of TBT and are also used as heat stabilizers in PVC. MBT, DBT and TBT are classified as persistent environmental pollutants; they degrade slowly in water but once accumulated in sediments they are stable. TPhT shows biocidal effects and is applied as a contact fungicide throughout the world to treat a variety of crops. Organotin compounds are included in the list of priority pollutants of the US Environmental Protection Agency (US-EPA) and the European Commission. In 1999, the US-EPA [2] recommended a maximum of  $10 \text{ ng L}^{-1}$  of TBT (as a cation) in seawater and  $63 \text{ ng L}^{-1}$  in freshwater, although recently it has established the ambient aquatic life water quality criteria for TBT (as cation) in which the criterion to protect saltwater aquatic life from chronic effects is  $7.4 \text{ ng L}^{-1}$  and  $420 \text{ ng L}^{-1}$  from acute toxic effects [3]. Meanwhile the European Environmental Quality Standard (EQS) of TBT for all types of waters covered by WFD is  $0.2 \text{ ng L}^{-1}$  for annual average concentration and maximum allowable concentration of  $1.5 \text{ ng L}^{-1}$  in unfiltered water samples [4]. Organotin compounds are bio-accumulable and relatively high levels of these compounds can be found in fatty tissues of exposed biota [5]. Measurement of the concentration of these pollutants in the water column is therefore important for assessing their potential long-term biological impact.

As the total concentration of organotin compounds in contaminated water is typically at the  $\text{ng L}^{-1}$  level, it is usually necessary to use large volumes of water and a pre-concentration step prior to analysis in order to achieve the required detection limit. A number of different pre-concentration and extraction methods has been used for the analysis of organotin compounds in water including: liquid–liquid extraction [6], supercritical fluid extraction [7], solid-phase extraction (SPE) [8] and solid-phase microextraction (SPME) [9]. Extracts are usually derivatized with sodium tetra-ethylborate ( $\text{NaBEt}_4$ ) and analysed by highly sensitive and selective instrumental techniques such as gas chromatography (GC) with flame photometric (FPD) [6] or inductively coupled plasma mass spectrometric (ICP-MS) [10] detection.

Both bio-monitoring (measurement of the accumulation of pollutants in tissues of living organisms) [11–13] or the collection of bottle, grab or spot samples of water [14] can be used to monitor levels of organotin compounds in the aquatic environment. The latter technique, however, provides information of the concentration of pollutants only at the time and point of sampling. Where levels fluctuate over short periods (e.g. tidal cycles, input of effluents) within a water body it is desirable to monitor over a longer time interval in order to obtain information on the time-weighted average (TWA) water concentration using for example the passive sampling devices.

The use of passive sampling techniques as an alternative strategy for monitoring water quality has been gaining considerable interest in recent years [15,16]. Passive sampling devices measure the freely dissolved (and usually bio-available) fraction of compounds in water and have a number of advantages over the use of spot sampling and bio-monitoring methods [17]. All passive sampling devices use a receiving phase with a high affinity for the analytes of interest. This phase is separated from the external aqueous environment by a diffusion

membrane. Pollutants in the water are sequestered by the receiving phase and accumulated. If the sampling rate of an analyte is known (usually determined using a flow-through calibration tank) the TWA concentration of a pollutant in the water column can be calculated. Devices can be deployed for short (days) or long (months) periods, are relatively low-cost, and can be used in a range of environments including sites that have limited security and/or are remote with little or no infrastructure.

A number of different devices are available for monitoring a wide range of priority pollutants including both organic and inorganic compounds; these have been recently reviewed [18]. Semi-permeable membrane devices (SPMD) are designed to sequester non-polar ( $\log K_{ow} > 3.0$ ) organic compounds, such as PAHs, PCBs and selected pesticides from water [19]. They have also been used to monitor concentration gradients of organotin compounds in seawater [10,12]. The Polar Organic Chemical Integrative Sampler (POCIS) [20] can be used for monitoring more polar ( $\log K_{ow} \leq 3.0$ ) hydrophilic organic compounds. For inorganic compounds the most commonly used sampler is the Diffusion Gradients in Thin films (DGT) [21] device and this has been used to measure TWA concentrations of most (e.g. Cd, Cu, Ni, Pb and Zn) heavy metal pollutants. Other designs include the Stabilized Liquid Membrane Device (SLMD) for sequestering toxic metal ions [22], and the Ecoscope for the simultaneous screening of both non-polar organics and metals [23]. In most cases the calibration data relating the amount of pollutant measured in the receiving phase back to their TWA concentrations are not available. Therefore, in some field applications data are reported only in terms of amounts of a chemical found in the device rather than the estimated TWA water concentration. Although this may be valuable information when investigating overall water quality, these data cannot be used for regulatory purposes such as required by the European Union's Water Framework Directive [4].

The Chemcatcher® passive sampler can be used to measure the TWA concentration of both organic [24,25] and heavy metal [26] pollutants in a range of aquatic environments. A common PTFE sampler body is used and selectivity and accumulation rates are regulated by the choice of the diffusion-limiting membrane and the receiving phase material employed in the different configurations of the device. Unlike other passive samplers currently available, the Chemcatcher® uses a solid, bound, receiving phase in the form of a 47 mm Empore™ disk. Recently a new configuration for the measurement of organotin compounds and inorganic mercury was developed and preliminary results have been reported [27]. For organotin compounds a combination of a  $\text{C}_{18}$  Empore™ disk as the receiving disk overlaid with a thin cellulose acetate (CA) diffusion limiting membrane was used. For the organotin compounds tested a linear uptake was obtained over the 14-day test period.

The aim of this study was investigate the effects of water temperature and turbulence on the sampling rate of organotin compounds and their stability once sequestered by the Chemcatcher®. The sampler was tested at a marine harbour site and the TWA concentrations obtained for the various organotin compounds were compared with those obtained with spot water sampling.

## 2. Theory of passive sampling

A number of reviews of the principles governing the uptake of an analyte by different designs of passive sampling device, including the Chemcatcher®, have been published [15,25,28]. The uptake kinetics of a chemical into a device can be described as an exponential approach to a maximum, and this can be divided into three stages: approximately linear, curvilinear and finally steady state. During initial deployment the accumulation rate is approximately linear, and during this period the mass of analyte in the receiving phase is dependent on the concentration to which the system has been exposed and the deployment time according to the relationship:

$$M_D = M_0 + C_W R_s t \quad (1)$$

where  $M_D$  is the mass (ng) of target analyte accumulated in the receiving phase over the deployment period,  $M_0$  the initial mass (ng) of the analyte in the receiving phase,  $C_W$  the TWA water concentration ( $\text{ng L}^{-1}$ ) over the deployment period,  $R_s$  the effective sampling rate of the device ( $\text{L day}^{-1}$ ) and  $t$  is the deployment time (days). The sampling rate ( $R_s$ ) is equivalent to the volume of water cleared per day by the device and is analyte specific, and is measured experimentally using flow-through calibration tanks under controlled conditions and at a fixed concentration ( $C_W$ ) of the analytes of interest. In the field, however,  $R_s$  is affected by variation in factors such as water temperature, turbulence, and biofouling of the diffusion membrane.

When the concentration of the analytes being sampled falls in the bulk water phase, material accumulated in the receiving phase can subsequently off-load. The rate of off-loading of preloaded performance reference compounds (PRCs) can be measured experimentally in the laboratory under the same conditions under which uptake parameters were determined. Here the receiving phase is loaded with a known amount of analyte and the device deployed in a test tank containing pure water ( $C_W = 0$ ). When off-loading follows first order exponential decay kinetics, then the amount of analyte originally loaded onto the disk and that remaining after the deployment are related as [29,30]:

$$m_D = m_{D(0)} \exp(-k_e t) \quad (2)$$

where  $m_D$  is the mass of the analyte in the receiving phase after deployment (ng),  $m_{D(0)}$  the mass of the analyte loaded originally in the receiving phase (ng),  $k_e$  the off-load exchange rate constant ( $\text{day}^{-1}$ ) and  $t$  is the time (days). This equation is a one-parameter equation, since the amount of compound initially spiked into the sampler ( $m_{D(0)}$ ) is always known.

If the relationship between uptake ( $R_s$ ) and off-load ( $k_e$ ) is linear, then an isotropic exchange is indicated. In this case it is possible to estimate the effective sampling rate ( $R_s$ ) in the field using the off-load exchange rate constant elimination ( $k_e$ ). Thus by measurement of  $k_e$  for a PRC such as an enriched isotope or deuterated analogue of the pollutant of interest under field conditions it is possible to calculate the equivalent values

of  $R_s$  according to the relationship [25,30]:

$$C_W = \frac{M_D - M_0}{R_s t} \quad (3)$$

## 3. Experimental

### 3.1. Chemicals and reagents

All solvents and reagents were of analytical grade or better purity. Ultrapure Milli-Q water (Millipore, OH, USA) was used throughout. All volumetric glassware had glass stoppers and was cleaned overnight with 10%  $\text{HNO}_3$  and rinsed several times with water before use. Tributyltin chloride (97%), dibutyltin dichloride (95%), monobutyltin trichloride (95%), triphenyltin chloride (95%) and tripropyltin chloride (95%) were from Alfa Aesar (Karlsruhe, Germany). Tripropyltin was commonly used as a chromatographic internal standard because it is easily derivatized and this organotin compound is not normally found in polluted water. All standard stock solutions ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving appropriate amounts of the organotin compounds in methanol (HPLC grade, SDS, Barcelona, Spain). Solutions were stored in glass bottles at  $4^\circ\text{C}$  in the dark. Working solutions were prepared daily by appropriate dilution of the stock solutions with methanol. An aqueous solution (1%, w/v) of  $\text{NaBEt}_4$  (98% Strem Chemicals, Bischoffheim, France) was used as derivatizing agent and was prepared in an acetic-acetate buffer ( $2 \text{ mol L}^{-1}$ , pH 4.6) media. The buffer was made by dissolving the appropriate amount of sodium acetate (99% Merck, Darmstadt, Germany) in acetic acid (99% Sharlab, Barcelona, Spain) and water to give a final volume of 1 L. Ethylated derivatives were extracted in *n*-hexane (Scharlab, Barcelona, Spain).

### 3.2. Passive sampler design

#### 3.2.1. Receiving phase disks

$\text{C}_{18}$  Empore™ disks (47 mm diameter) were from 3M (Bioanalytical Europe, Neuss, Germany). The disks were pre-conditioned by soaking in methanol for 30 min until translucent and then rinsed several times with water. The disks were not allowed to dry out between conditioning and use. The disks were found to be free of contamination by the organotin compounds under investigation.

#### 3.2.2. Diffusion membranes

CA ( $0.45 \mu\text{m}$  pore size) membranes were from Pall Europe (WWR International, S.L. Mollet del Valles, Spain) and were also found to be free of contamination by the organotin compounds under investigation. These membranes did not need neither a washing or a pre-conditioning step.

#### 3.2.3. Chemcatcher® sampler

Sampler bodies that retain both the receiving phase and diffusion membrane were made of PTFE. The sampler design has been described in detail elsewhere [25–27]. The CA diffusion membrane (47 mm diameter) was placed on the top of the conditioned  $\text{C}_{18}$  Empore™ disk, and care was taken to avoid formation of air bubbles between the two layers. Once

the sampler was assembled, the cavity in front of the diffusion membrane was filled with water and then sealed until use by a PTFE cap and locking ring. The PTFE was shown to be free of contamination by organotin compounds.

### 3.3. Flow-through exposure tank calibration experiments

The flow-through exposure tank was similar to that described by Vrana et al. [25]. It consisted of a glass tank (31.5 cm × 38 cm × 40 cm) with an overflow to waste and was kept in the dark. For the uptake experiments tap-water (found to be free of contamination by the organotin compound under investigation) was fed (30 mL min<sup>-1</sup>) into the tank using a peristaltic pump (Watson Marlow Model 323 E, Falmouth, UK) together with a separate solution of organotins fed (0.3 mL min<sup>-1</sup>) using second peristaltic pump (Minipuls Gilson, Villiers-le-Bel, France). A nominal concentration (400 ng L<sup>-1</sup>) of each organotin compound was maintained throughout. In order to keep homogeneous conditions the water was stirred (RZ1 overhead stirrer, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) at 40 rpm. In order to allow the system stabilise it was operated for a minimum of 48 h before the samplers were deployed. A refrigeration unit (FRIGEDOR 3001214, P Selecta, Barcelona, Spain) was used to control the water temperature in the tank. Pre-cleaned PTFE tubing (0.6 mm i.d.), Tygon tubing (0.6 and 1.6 mm i.d.) and Omnifit connectors (all from AFORA, Madrid, Spain) were used to connect the different components of the system together. Tap-water used for the calibration experiments had on average a conductivity of 143 μS cm<sup>-1</sup> at 20 °C, a pH 7.45 and contained: Ca (34.9 mg L<sup>-1</sup>), K (0.5 mg L<sup>-1</sup>), Mg (8 mg L<sup>-1</sup>), Na (1.8 mg L<sup>-1</sup>) and Cl<sup>-</sup> (38 mg L<sup>-1</sup>).

A PTFE carousel (made at University of Portsmouth, Portsmouth, UK) was used to hold the samplers and it is described elsewhere [25]. The carousel comprised two horizontal turntables and a supporting rod that was connected to an overhead stirrer. Each turntable held up to 7 samplers, so that 14 samplers could be exposed simultaneously in each experiment. Three different levels of water turbulence were simulated in the uptake and off-load studies. Stirring level (SL) 1 was achieved by placing the samplers at the bottom of the tank facing upwards, and placing the overhead stirrer in the middle of the tank at a depth of 20 cm and rotating it at 40 rpm. SL2, and SL3 corresponded to the samplers loaded in the carousel being rotated at 40 rpm and 70 rpm, respectively.

In order to determine the accumulation or desorption rates of organotins during uptake or off-loading experiments, 14 samplers were placed in the carousel and deployed for up to 14-day in the tank. The off-load experiments were carried out by loading the C<sub>18</sub> disk with 500 ng of each organotin compound. This was achieved by slowly filtering an aqueous solution (100 mL, 5 μg L<sup>-1</sup>) of each compound through the disk. After loading, disks were dried (15 min) under vacuum to remove excess water. The disks were loaded into the samplers and exposed in organotin free tap-water using conditions similar to the uptake experiments above. Three samplers were used to determine the initial mass of organotin present in the receiving disk before the experiments and two samplers were used as fabrication blanks. The recovery rates of the analytes for the loaded procedure was 95 ± 6 for each analyte.

During deployment, two or three replicate samplers were retrieved after 2, 5, 8, 11 and 14 days of exposure and the amount of organotin accumulated or remaining in the receiving disks was determined. Every time a sampler was removed it was replaced by a dummy sampler body (without a disk and membrane). This was necessary to preserve constant hydrodynamic conditions within the calibration system. Duplicate water samples were taken daily from the outlet of the tank to measure the concentration of organotins during the exposure study. Throughout the studies the concentration of the organotin compounds in the water of the tank was in the 360–470 ng L<sup>-1</sup> range for the 14 days calibration experiments. The different exposure conditions are summarised in Table 1.

### 3.4. Extraction of organotin compounds from the receiving phase, derivatization procedure and instrumental conditions

Organotin compounds were extracted from the C<sub>18</sub> disk with methanolic acetic acid 1:3 mixture (8 mL, 13 mol L<sup>-1</sup>) in an ultrasonic bath (10 min) [25]. Organotin compounds must be derivatized (usually by ethylation with NaBEt<sub>4</sub>) to form more volatile species prior to analysis by GC-ICP-MS. Water samples (100 mL, both spot samples taken from the tank and field site) and sampler extracts (8 mL), together with the internal standard tripropyltin (TPrT) to give a final concentration of 70 μg L<sup>-1</sup> (as tin), were mixed with acetic-acetate buffer (2 mL; 2 mol L<sup>-1</sup>; pH 4.6), *n*-hexane (1 mL) and 1% NaBEt<sub>4</sub> (1 mL). The mixture was mechanically shaken (10 min) and the organic layer carefully transferred to an amber glass vial (4 mL) for analysis.

**Table 1 – Conditions used in the flow-through tank calibration experiments for the calculation of uptake rates and off-load rates of organotins**

Calibration experiment number	1	2	3	4	5	6	7	8
Water temperature (°C)	4	4	11	11	11	18	18	18
Carousel rotation speed (rpm)	40 (SL2)	70 (SL3)	– (SL1)	40 (SL2)	70 (SL3)	– (SL1)	40 (SL2)	70 (SL3)
Estimated linear water velocity <sup>a</sup> (cm s <sup>-1</sup> )	40	70	–	40	70	–	40	70

–: No carousel was employed. SL1: samplers deployed at the bottom of the calibration tank. SL2: samplers rotating at 40 rpm. SL3: samplers rotating at 70 rpm.

<sup>a</sup> Linear velocity was calculated as  $2\pi rf$ , where  $r$  is the radius between the centre of the calibration carousel and the centre of the sampler and  $f$  is the rotation speed.



Analysis of ethylated MBT, DBT and TBT was performed by GC–ICP–MS (ICP–MS, model HP-4500 and GC model HP-4890, Agilent Technologies, Bracknell, UK). The GC was interfaced to the ICP–MS by a PTFE tube (80 cm long and 1.5 mm i.d.) heated to 250 °C [31]. The GC was fitted with a non-polar fused silica capillary column HP-5 (cross-linked 5% phenylmethylsilicone, 15 m long  $\times$  0.32 mm i.d., with a 0.25  $\mu$ m film thickness, Agilent Technologies, Spain) and operated under the following conditions: splitless injection mode; injection port temperature 250 °C; injection volume 1  $\mu$ L; oven temperature programme: 50 °C (0.5 min) then 30 °C min<sup>−1</sup> to 250 °C (1 min). The ICP–MS was operated at a power (RF) of 1350 W with a carrier gas flow-rate of 1.2 L min<sup>−1</sup>. Data were collected by monitoring ions (0.2 s integration time per isotope) at  $m/z$  = 118, 119 and 120 specific for the tin. The ICP–MS was tuned using ion  $m/z$  = 126, corresponding to the xenon present in the argon plasma gas. Due to its high boiling point, TPhT cannot be measured by GC–ICP–MS as it condenses in the interface transfer line. For the analysis of TPhT, GC–FPD (HP-5890, Agilent Technologies, Spain) with the cut-off filter set at 610 nm (for tin species) was used. Chromatographic conditions were as the GC–ICP–MS analysis.

### 3.5. Stability studies

A stability study of the organotin compounds in the C<sub>18</sub> disks and spot water samples under different storage conditions was performed. For this experiment 24 Chemcatchers® were exposed to 5  $\mu$ g L<sup>−1</sup> each test analyte at 18 °C and stirring level SL1 for 2 days in the flow-through tank. The disks were removed and stored under different conditions that simulated sampler retrieval, transport to the laboratory and storage before analysis. The storage conditions tested were different combinations of refrigeration at 4 °C and freezing at −18 °C.

The analyte accumulated in samplers was analysed after 0, 3, 7 and 10 days of storage. In addition, the stability of 24 water samples collected from the flow-through tank and stored in amber glass bottles after the addition of acetic acid (1 mL L<sup>−1</sup> of water) for stabilisation was determined under analogous storage conditions.

### 3.6. Field trial and analysis of water samples and passive samplers extracts

Six Chemcatcher® samplers fitted with C<sub>18</sub> disks and CA diffusion membranes were attached to a metal bar, by means of a nylon line, in close proximity to each other and deployed in Alicante commercial harbour on the Mediterranean Sea (Spain) during 1–15 November 2005. The samplers were suspended at a depth of 1 m with the diffusion membrane surface horizontal and facing downwards to minimize the accumulation of sediments. After deployment the samplers were retrieved, filled with water from the sampling site (to avoid the receiving phase drying out), sealed and kept refrigerated during transport to the laboratory. Once in the laboratory the disk was removed from each sampler and stored at −18 °C until analysis. Two samplers were prepared to act as field blanks to assess contamination during transport (to and from the field) and during deployment and retrieval of the devices.

Three replicate spot water samples (500 mL) were taken from the field site on six occasions (days: 1 (deployment), 2, 4, 8, 11, 14) during the 14-day trial and stored in clean amber glass bottles with 0.5 mL of acetic acid added for stabilisation. Samples were refrigerated during transport to the laboratory. All water samples were stored at 4 °C until analysis and were analysed directly without filtration. These procedures are comparable with those used in regulatory monitoring. Water temperature during the deployment was 17–19 °C.

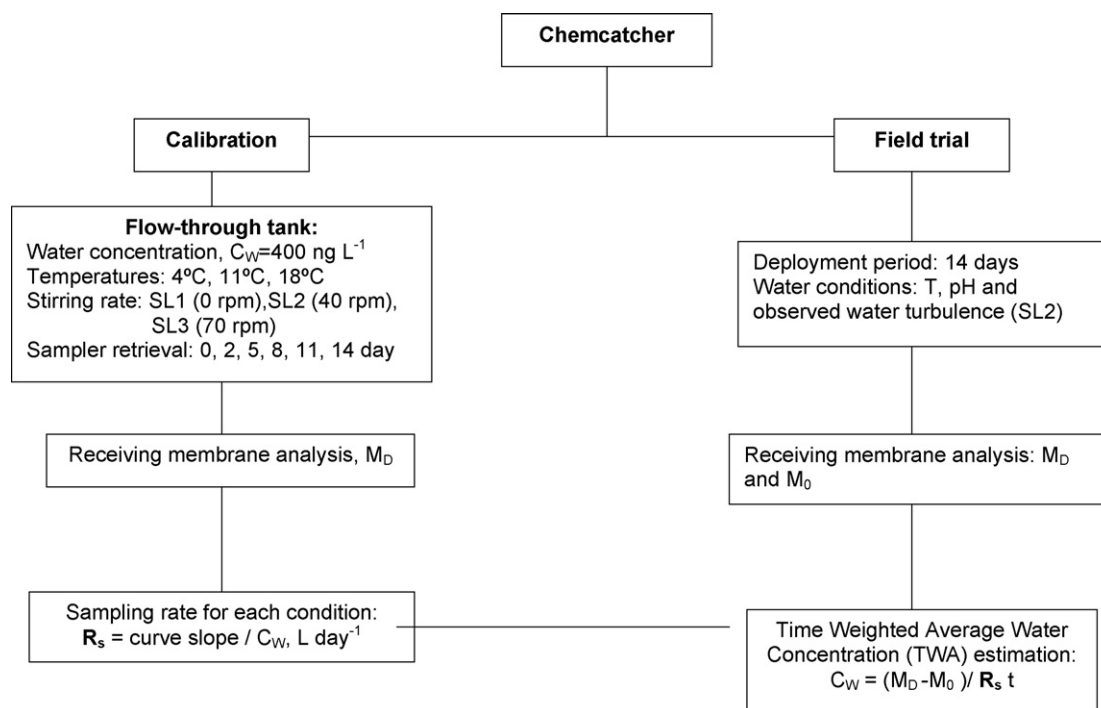


Fig. 1 – Diagram presenting the analytical protocol for calibration and field trial studies.

Fig. 1 shows a diagram presenting the whole analytical protocol for calibration and field trial studies.

## 4. Results and discussion

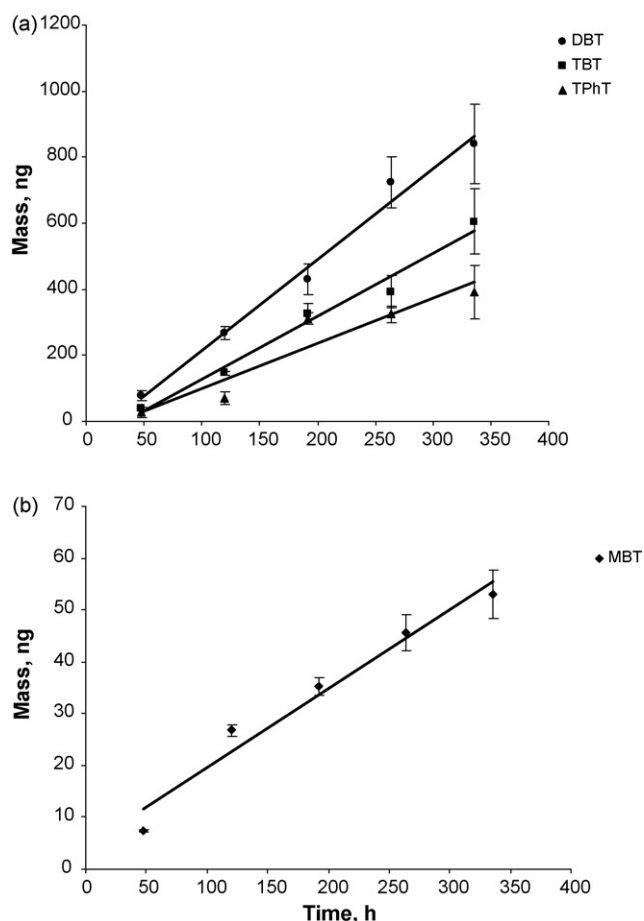
### 4.1. Uptake and off-load rates of organotin compounds in the tank studies

To determine the TWA concentration of organotin compounds in water it is necessary to know the compound-specific sampling rate ( $R_s$  expressed as  $\text{mL day}^{-1}$ ) for the prevailing environmental conditions. For most non-polar compounds sampling rates are affected by water temperature, turbulence and degree of biofouling on the surface of the diffusion membrane [15]. The uptake is affected by two diffusion barriers: the unstirred water boundary layer and the diffusion membrane. In more turbulent conditions the thickness of the boundary layer decreases (typically 1 mm in stagnant conditions and 0.001–0.1 mm in fast flowing waters). Hence, if the mass transfer is controlled by diffusion in the water boundary layer, the sampling rate increases with increasing water turbulence [24]. The rate of diffusion (and hence uptake) also increases with temperature [21,25].

In order to better understand how these variables affect the performance of the Chemcatcher® for the uptake of organotin compounds, samplers were deployed in the calibration tank for up to 14 days at different water temperatures and levels of turbulence using a full factorial design (Table 1). Each factor (water temperature and stirring speed) was tested at three different levels at a constant concentration ( $C_w$ ) of test compound and the amount of analyte accumulated in the receiving disk ( $M_D$ ) was measured. In most experiments satisfactory linear regression fits of Eq. (1) were obtained for all compounds; examples of the characteristic uptake curves are shown in Fig. 2.  $R_s$  of test compounds at each stirring and temperature experiment condition tested were calculated from the slopes of the calibration curves and the nominal aqueous analyte concentrations during the corresponding exposure period (Table 2).

The lag-time could be due to either the delay caused by the slow diffusion of an analyte across the rate limiting barriers, and/or the time taken to saturate binding sites in the diffusion limiting membrane before breakthrough is achieved. This lag-time depends on experimental conditions. A long delay between exposure and accumulation in the receiving phase implies that the sampler would not be responsive to short-term fluctuations in environmental concentrations. A long lag-time was observed at 4 °C and low turbulence (SL1 stirring speed). This resulted in a rate of accumulation of analytes that was too low to permit the establishment of an uptake curve. At 11 °C and SL1 the lag-time was higher than 5 days. At higher turbulence levels (SL2 and SL3) the lag-time was always less than 1-day. In most field applications of the device the water flow will be turbulent (i.e. SL2 or SL3 conditions) with a temperature in the range of 10–20 °C and therefore the  $R_s$  values obtained in these calibrations can be applied.

Fig. 3 shows the combined effect of water temperature and turbulence on the  $R_s$  for each organotin compound. No important differences can be found between 11 °C and 18 °C



**Fig. 2 – Uptake curves of (a) tributyltin (TBT), dibutyltin (DBT) and triphenyltin (TPhT), and (b) monobutyltin (MBT) for the Chemcatcher® deployed in a flow-through calibration tank. Water temperature 18 °C and turbulence condition SL2 (carousel rotation speed 40 rpm). Nominal concentration of each compound was 400  $\mu\text{g L}^{-1}$  ( $n = 3$ ).**

at the same stirring level taking into account the measurement error. An increase in water temperature in the range of 4–11 °C increases the sampling rate, and this particularly marked at SL2. This is in general agreement with the temperature sensitive behaviour of non-polar organic compounds [15,24,25]. Other temperature dependent factors that can affect  $R_s$  include changes in water viscosity affecting diffusion across bulk water and pore water in the diffusion membranes, and in the energy of interaction between the test compounds and the receiving phase.

As expected water turbulence had an important effect on the sampling rate for all four organotin compounds and was most marked for TPhT, the least polar test analyte (Fig. 3d). At 11 °C and 18 °C the sampling rate increased with stirring speed. For non-polar organic compounds, similar effects have been reported for the SPMD [29] and Chemcatcher® [24] passive samplers. These results suggest that accumulation was mainly affected by diffusion through an aqueous boundary layer, and to a lesser extent by diffusion across the CA membrane.

**Table 2 – Chemcatcher® sampling rates ( $R_s$ ) for organotin compounds in the flow-through tank calibration experiments at different water temperatures and levels of simulated water turbulence**

Organotin compound	Stirring level (degree of water turbulence)	Sampling rate, $R_s$ (mL day <sup>-1</sup> )		
		Water temperature		
		4 °C	11 °C	18 °C
TBT	SL1	<sup>a</sup>	29 ± 12	56 ± 17
	SL2	42 ± 11	117 ± 27	106 ± 25
	SL3	174 ± 36	201 ± 21	202 ± 28
DBT	SL1	<sup>a</sup>	41 ± 25	48 ± 14
	SL2	45 ± 8	137 ± 34	141 ± 36
	SL3	129 ± 22	189 ± 32	204 ± 28
MBT	SL1	<sup>a</sup>	6 ± 2	4 ± 1
	SL2	3 ± 1	18 ± 5	11 ± 3
	SL3	23 ± 7	22 ± 5	18 ± 7
TPhT	SL1	<sup>a</sup>	26 ± 9	38 ± 12
	SL2	32 ± 8	60 ± 15	59 ± 19
	SL3	160 ± 33	191 ± 29	173 ± 28

Results are expressed as mean  $R_s$  ± coefficient of variation ( $n=3$ ). Key: TBT: tributyltin; DBT: dibutyltin; MBT: monobutyltin; TPhT: triphenyltin. SL1: samplers deployed at the bottom of the calibration tank. SL2: samplers rotating at 40 rpm. SL3: samplers rotating at 70 rpm.

<sup>a</sup> Due to the long lag-phase under these conditions the sampling rate was not measured.

The equivalent sampled volumes ( $R_s \times$  deployment time) in flowing water (SL2 and SL3) at 11 or 18 °C over typical 14-day deployment were in the range of 1.5–2.8 L for TBT, 1.9–2.9 L for DBT, 0.15–0.31 L for MBT and 0.8–2.7 L for TPhT. Except for MBT, there is a good pre-concentration of the organotins in the receiving phase disk under these conditions, and this permits the device to be used to monitor these compounds in the aquatic environment.

Off-loading behaviour was assessed by pre-loading 500 ng of each test analyte on to the  $C_{18}$  disk and exposing the sampler in the tank under the same conditions for the calculation of sampling rates (Table 1), but using unspiked tap-water ( $C_w=0$ ). Fig. 4 shows the off-loading kinetic profiles for TBT and DBT at 18 °C and SL2. Similar profiles were obtained for MBT, TPhT and other temperatures and turbulence levels. A rapid off-loading over the first 48–96 h (about a 20–30% of the initial amount loaded on to the disk) occurred and then a steady state was reached with no more off-loading. The off-loading after 14-day of deployment varies between 10 and 38% depending on the analyte and the conditions. Typically up to 70% of the compound remains on the disks. One explanation for this behaviour could be that the receiving phase was not homogeneous leading to the existence of two binding mechanisms for the organotins. This could lead to one fraction being easily desorbed from the disk (fraction lost after 48 h of deployment), and the other fraction being strongly adsorbed. This behaviour was consistent throughout the series of off-load calibration experiments and precluded the application of either a first order exponential regression model or a linear model for the estimation of  $k_e$ . This anisotropic exchange behaviour does not allow the use of the PRC approach to correct  $R_s$  for fluctuations in environmental conditions over the deployment period. Additional studies are required to understand and model this apparent biphasic off-loading process.

#### 4.2. Limits of detection for the Chemcatcher®

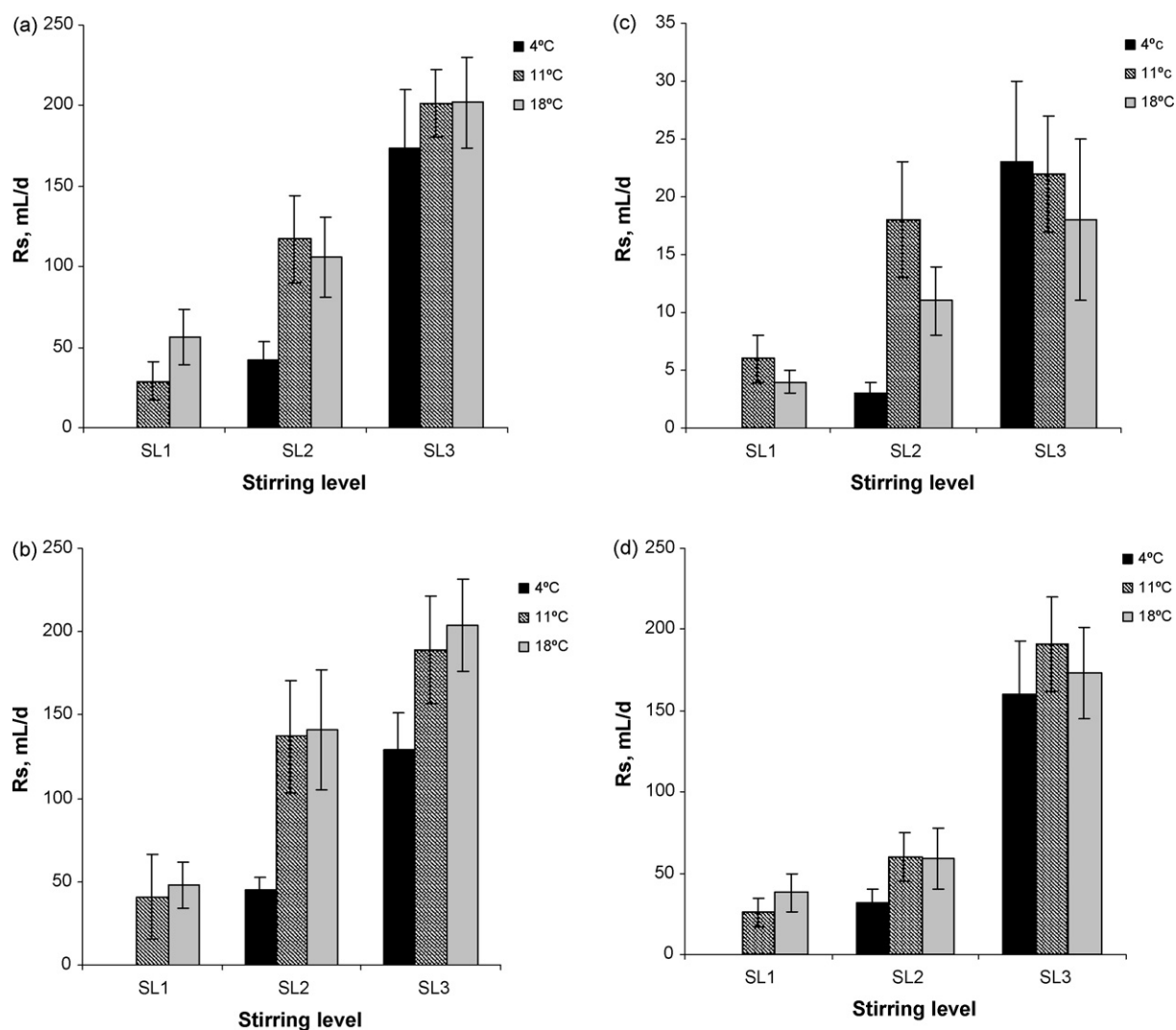
The detection and quantification limits for environmental pollutants depend on the sampling rate (and hence water temperature and turbulence) and the exposure period. The overall method detection limit (MDL), was calculated as the minimum aqueous concentration ( $C_w$ ) of organotin detectable by the sampler after a typical 14-day field exposure. This was calculated by substituting into Eq. (1) the GC-ICP-MS and the GC-FPD instrumental detection limits for a blank sampler (calculated as three times the standard deviation based on 10 replicates) in the mass accumulated ( $M_D$ ) term, and using the different sampling rates ( $R_s$ ). The minimum quantification limit (MQL) was also calculated by substituting the instrumental quantification limits, calculated as 10 times the standard deviation based on 10 replicates, into Eq. (1). The MDL and MQL for the organotin compounds are shown in Table 3. In general the MQL values obtained were low enough

**Table 3 – Limits of detection and quantification for the Chemcatcher® passive sampling device calculated at the different temperatures and turbulences tested over a 14-day deployment**

Organotin compound	MDL <sup>a</sup> (ng L <sup>-1</sup> )	MQL <sup>a</sup> (ng L <sup>-1</sup> )
TBT	0.3–2.1	0.8–7
DBT	0.2–1	0.8–3.5
MBT	1.0–5.6	3.3–19
TPhT	1.4–7.5	4.6–25

The lower value corresponds to 18 °C, SL3 and the upper value to 4 °C, SL2 and/or 11 °C SL1. Key: TBT: tributyltin; DBT: dibutyltin; MBT: monobutyltin; TPhT: triphenyltin

<sup>a</sup> MDL and MQL are the method detection limit and minimum quantification limits, respectively ( $n=10$ ).



**Fig. 3** – Effect of water temperature and simulated water turbulence on the Chemcatcher® sampling rate ( $R_s$ ). (a) tributyltin (TBT), (b) dibutyltin (DBT), (c) monobutyltin (MBT) and (d) triphenyltin (TPhT). Nominal concentration of each compound was  $400 \mu\text{g L}^{-1}$ . The error bars on the graphs represent the calculated variation coefficient for  $R_s$  ( $n = 3$ ).

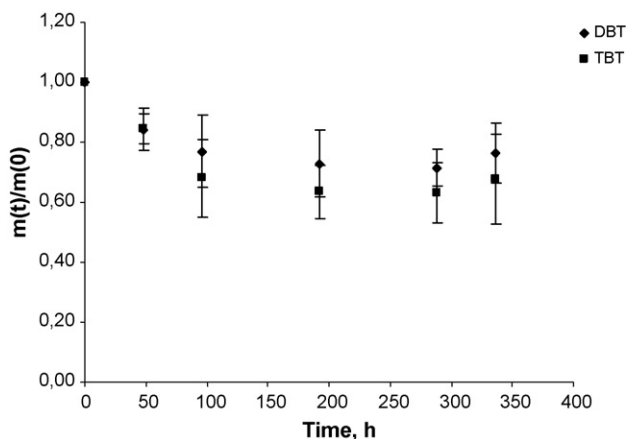
for the determination of these compounds in slightly contaminated waters (with an average TBT content in the range of  $4\text{--}80 \text{ ng L}^{-1}$ ) [32]. Even, these MDL and MQL values were higher to those reported by Ariza et al. [33] or González-Toledo et al. [8] by the processing of 1 L and 250 mL sample, respectively. These quantifications limits were lower than the maximum levels recommended by US-EPA. Although according to WFD, the method quantification limit for TBT should be 30% of EQS value, i.e.  $0.3 \times 0.2 \text{ ng L}^{-1} = 0.06 \text{ ng L}^{-1}$ . Such a low limit cannot be easily obtained either by recently used spot sampling methods or Chemcatcher®. For spot sampling, the achievement of the recommended detection limit implies the processing of several litres of water and the application of an extreme control of reagents and glassware cleaning to minimised blanks values, with an accurate and high sensitive method such as isotope dilution [14]. For the Chemcatcher®, as well as of an improvement on determination methods (blank control, increase signal to noise ratio, etc.), some measures on sampler design such as an increase on sampler surface, the application

of pool extracts from several samplers together, an additional preconcentration step of this pool extract or even an increase of exposure period, would make the method suitable for EQS compliance monitoring.

#### 4.3. Stability studies

Organotin compounds can be unstable in water at low  $\text{ng L}^{-1}$  concentrations [35,36]. Therefore, it was important to assess the stability of the sequestered organotin compounds in bottle samples, and on the receiving phase of the Chemcatcher®. Recoveries at  $t=0$  days (without storage) were nominally set at 100%, and no significant losses (TBT: 106%, DBT: 95%, MBT: 106% and TPhT: 90%) of organotins from  $\text{C}_{18}$  disks were found over the storage period (10 days) under the conditions of 3 days refrigeration at  $4^\circ\text{C}$  followed by 7 days freezing at  $-18^\circ\text{C}$ . These results show that after field retrieval, the disks can be safely stored in the laboratory for over 1 week before subsequent analysis. For comparison the stability of organotin



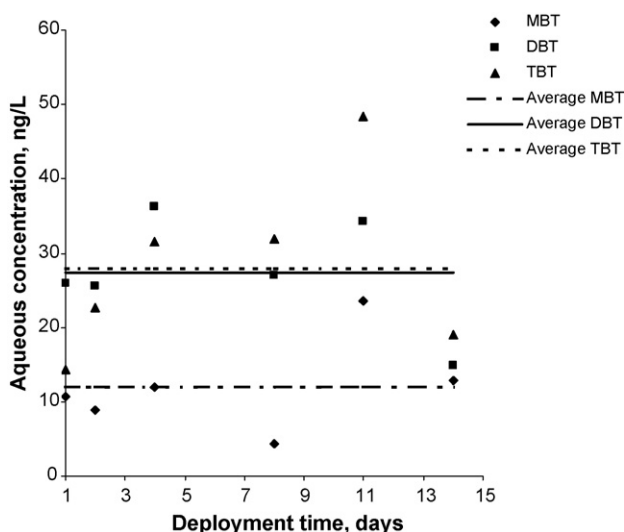


**Fig. 4 – Off-load curves for tributyltin (TBT) and dibutyltin (DBT) from the Chemcatcher®.** Water temperature 18 °C and turbulence condition SL2 (carousel rotation speed 40 min<sup>-1</sup>). A 500 ng of each compound (as tin) was pre-loaded on the C<sub>18</sub> Empore™ disk at the start of the experiment. Key:  $m(t)$  = mass remaining in the disk at time (t) and  $m(0)$  = mass originally loaded in the disk.

compounds in water acidified in the field with 0.1% (v/v) acetic acid was measured after storage for 7 days at 4 °C, and again no appreciable losses of analyte was detected.

#### 4.4. Field trial in Alicante Harbour

MBT, DBT and TBT were found in all spot water samples taken during the field trial, but their concentrations fluctuated markedly over the 14-day period (Fig. 5). As expected,



**Fig. 5 – Concentration of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) measured in spot water samples collected from Alicante Harbour, Spain during the Chemcatcher® deployment period.** The lines represent the arithmetic mean concentration (of the six sampling times) of the three-organotin compounds over the 14-day deployment period.

TPhT was not found in water at the harbour site, as this substance is mainly used for agricultural purposes. Temporal variation in the aqueous concentrations was reflected in the high relative standard deviations (ranging between 24 and 50% depending on the analyte) obtained for the mean water concentration measured in the six bottle samples. Such fluctuations are typical for a partly enclosed harbour site, and were probably due to tidal flushing and movement of boats which redistribute organotin compounds in the bottom sediment into the water column. The levels (mean value: 28 ng L<sup>-1</sup>, 27 ng L<sup>-1</sup> and 12 ng L<sup>-1</sup> for TBT, DBT and MBT, respectively) found are consistent with or lower than those found in other moderately contaminated European harbours [33–38].

Shipping activity is responsible for the TBT found in the harbour. This compound has been used in antifouling paints that are applied to protect the hulls of large vessels. In general, TBT levels in harbour areas with a high degree of shipping activity are higher than those found for DBT and MBT [33]. However, input of TBT from antifouling paints has fallen and continues to fall due to the implementation of new environmental legislation governing the use of this substance for this purpose. As a result the relative levels of its associated breakdown products, DBT and MBT are expected to increase in the environment with time. The ratio between the total concentration of these two degradation products and TBT is used to estimate the fate of this compound and to assess the temporal variability of the inputs. This relation is known as butyltin degradation index (BDI) [37]:

$$\text{BDI} = \frac{[\text{MBT}] + [\text{DBT}]}{[\text{TBT}]} \quad (4)$$

In this study a BDI value of 1.4 was found based on the mean concentrations in the spot water samples (Fig. 5). This implies a significant degradation of TBT, without any recent inputs of this compound. This degradation is confirmed by the similarity between the levels of DBT and TBT. Also MBT data follows the general trend reported which implies slower degradation from DBT [34–38].

After the 14-day deployment of the Chemcatcher® in the harbour, the upper surface of the body was covered in a thin film of silt. Only a small degree of biofouling by bacteria and algae was found on the surface of the CA diffusion-limiting membrane. Table 4 shows the mass of each organotin accumulated in the receiving phase of the Chemcatcher® over the deployment period. For the three-organotin compounds detected, the variation in the masses accumulated by the six replicate devices was in the range of 15–28%, implying a good reproducibility across the devices.

The water temperature at the harbour during the deployment was on average 18 °C, and the water turbulence was estimated as equivalent to a stirring speed of SL2. The TWA concentrations of the organotins were then estimated by using the corresponding  $R_s$  value (Table 2) and Eq. (3). Although the laboratory calibrations were carried out in tap-water, the parameters can be used in seawater since salinity has been shown to have no effect on the uptake rates of organotins [27]. Over the trial, under these conditions, the Chemcatcher® sampled the equivalent of 1.48, 1.97 and 0.15 L of the water for TBT, DBT and MBT, respectively. The estimated TWA concen-

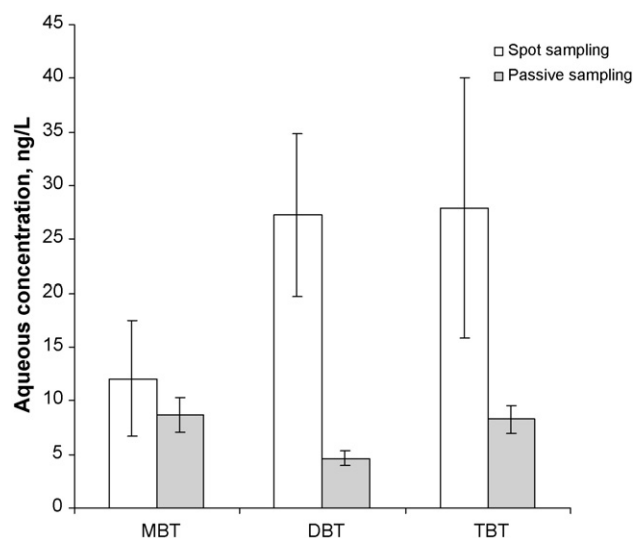
**Table 4 – Mass of organotin compound accumulated in the C<sub>18</sub> Empore™ receiving phase disk of the Chemcatcher® after a 14-day deployment in the Alicante Harbour (Spain)**

Sampler number	TBT (ng)	DBT (ng)	MBT (ng)
1	10.7	7.5	1.4
2	9.4	7.6	1.1
3	13.6	9.0	1.0
4	14.4	10.5	0.9
5	12.5	9.8	1.8
6	12.9	10.5	1.8
Mean ± S.D.	12.3 ± 1.9	9.2 ± 1.3	1.4 ± 0.4

Laboratory and field blanks were below detection limit for all analytes. Key: TBT: tributyltin; DBT: dibutyltin; MBT: monobutyltin; TPhT: triphenyltin. S.D.: standard deviation (n=6).

trations for TBT, DBT and MBT were 8.3 ng L<sup>-1</sup>, 4.6 ng L<sup>-1</sup> and 8.7 ng L<sup>-1</sup>, respectively. These values yielded a 1.6 BDI value, similar to that obtained for spot samples. Fig. 6 shows the comparison between the TWA concentrations obtained with the passive sampler and mean water concentrations obtained by spot sampling for the three organotin compounds. The TWA concentrations were lower than those values measured in spot samples. Such differences are common for most of passive sampling devices [15]. There is a number of possible reasons for this observation.

Firstly, the measurement of the concentration of pollutants in unfiltered spot water samples includes the free or truly dissolved fraction of a chemical, and also the fraction bound to particulate and dissolved organic matter. However, most passive samplers sequester only the freely dissolved (and hence bio-available) fraction of a chemical, and that fraction



**Fig. 6 – Time-weighted average (TWA) concentrations measured by the Chemcatcher® (n = 6) compared with the arithmetic mean water concentrations found in spot water samples collected over the 14-day field trial in Alicante Harbour. The bars on the data represent the range of values found over the trial period. Key: monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT).**

that is able to diffuse through the pores of the diffusion-limiting membrane. The pore size of the CA membrane used was 450 nm, and hence truly dissolved organotin compounds and some of that complexed with dissolved organic material (depending on size) can be accumulated in the receiving phase. It has been reported that up to 95% of TBT in the water column is bound to suspended particles. The remainder is either freely available or associated with dissolved organic and inorganic ligands [5]. As the hydrophobicity of the organotins increases the proportion associated with dissolved organic matter will increase, and hence the amount sampled by the device will be increasingly dependent on the size of those complexes and their ability to diffuse across the membrane to reach the C<sub>18</sub> receiving phase. In seawater (pH ≈ 8.0) it is assumed that a large fraction of TBT, and even DBT, would be in a non-dissociated form [36]. This favours their binding to organic matter, thus reducing the freely dissolved fraction that is readily available for sequestration by the Chemcatcher®. Due to its more hydrophilic properties, a greater fraction of MBT is truly dissolved (and hence more bio-available). This is consistent with the smaller differences found between the estimated TWA concentration and the average measured in spot water samples.

Secondly, as the concentration of organotin compounds in the harbour varied so widely over the monitoring period, the mean of the concentrations in six spot samples over a 14-day period may not provide a representative reflection of the true TWA concentration [13,16]. Among the different passive samplers designs available, only the triolein-filled SPMD [10,12] and dialysis bags filled with n-hexane [38] have been used to measure organotin compounds in water. However, unlike the Chemcatcher® sampler, these devices were not calibrated for these analytes, and up to now their usage has been limited to indicating the spatial variation of these compounds in the water column in enclosed areas and in sediment pore water. These devices are designed to accumulate non-polar pollutants, and are less well suited to more polar analytes. Consequently they accumulate MBT to a lesser extent than the more hydrophobic organotins.

## 5. Conclusions

A new version of the Chemcatcher® passive sampler that uses a C<sub>18</sub> chromatographic phase as receiving disk overlaid with a CA diffusion-limiting membrane has been developed and a calibration database established to enable its use as an integrative sampling tool to monitor selected organotin compounds in water. The sampler is simple to use and deploy and compared with most other designs of passive sampler, the receiving phase material is easy to analyse using existing laboratory protocols. The effect of two main environmental variables, water temperature and water turbulence, on the sampler performance was characterised. The comparison of the uptake and off-loading behaviour of the test analytes showed anisotropic exchange kinetics, and so it was not possible to use the PRC approach for in situ calibration.

The sampling rates obtained were sufficiently high to enable this sampler to be used for measuring TWA concen-

trations of organotins in most polluted aquatic environments. The amounts of these compounds accumulated in the receiving phase over the deployment period were sufficient to bring them within the limits of quantification of the analytical methods used in this study. This combined with the representative information on concentration over a period of time, even where there are temporal fluctuations, make this method potentially useful as a cost effective tool for use in the context of regulatory monitoring. A further advantage is that the Chemcatcher® measures the concentration of the dissolved (biologically relevant) fraction of the organotins. The use of unfiltered spot water samples (as defined in regulatory methods) can give biased pictures of TBT levels where sediment can become intermittently resuspended by for instance the movement of boats or tidal currents. Under these circumstances the timing of the sampling event could have a marked effect on the concentration found. This passive sampler extends the range of tools available to those with responsibility for monitoring the quality of surface waters.

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